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Reactions of XeF_2 and ~~Me_3SiN_3~~ at low temperatures gave ~~Me_3SiF~~ and possibly $Xe(N_3)_2$ as indicated by subsequent decomposition to Xe and N_2. These reactions were erratic in either solventless or ~~CF_2Cl_2~~ solvent systems. Trapping the azide radical from the decomposition with a fluoroolefin was not realized. The interaction of ~~$KClO_3$~~ and ~~Me_3SiCl~~ gave ~~KCl~~ but the expected Me_3SiClO_3 was not isolated. It was not possible to duplicate the claimed synthesis of nitryl azie from alkali metal azides and ~~NO_2BF_4~~. An alternate synthesis of ~~NO_2N_3~~ from HN_3 and ~~FNO_2~~ in anhydrous HF apparently resulted in an equilibrium involving ~~NO_2N_3~~ and NO_2HF_2. Pentafluorosulfuroxide containing fluorocarbons were prepared by addition of SF_5OCl to unsymmetrical fluoroethylenes and also by the addition of SF_5OF to $CFCl{=}CFCl$. These new compounds were thoroughly characterized. Numerous unsuccessful attempts were made to dehalogenate $SF_5OCFClCF_2Cl$ and $SF_5OCFBrCF_2Cl$ using zinc and other reducing agents in a variety of solvents and without solvent. Perfluorovinyl cadmium iodide was prepared in DMF solvent and reacted with FNO_2. However this did not furnish any of the desired $CF_2{=}CF(NO_2)$

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resulting instead in the generation of the dimer derivative perfluorobutadiene and small amounts of $CF_3CFH(NO_2')$. The cadmium reagent was also converted to the mercury species CF_2=CF-Hg-Cl which also did not yield CF_2=$CFNO_2$ on reaction with FNO_2. Perfluorovinyl cadmium iodide could not be synthesized in THF solvent and the alternate nitrating agent, NO_2BF_4, was not compatible with DMF.

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BASIC RESEARCH IN ENERGETIC FLUOROCARBONS

FINAL REPORT

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Final Report for the Period 1 March 1985 to 31 December 1986

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A

SUMMARY

During this program two areas from the diverse planned effort were the subject of investigation. The first of these involved the synthesis of new transfer agents for energetic substituents. Among the new agents sought was $Xe(N_3)_2$. Efforts to prepare this compound centered on solvent free reactions and CF_2Cl_2 solvent reactions of solid XeF_2 and liquid trimethyl silyl azide. At -78 to -60C it was found that the expected by-product, Me_3SiF, was generated slowly, accompanied by only small amounts of Xe and N_2, the projected decomposition products of $Xe(N_3)_2$. Above -60C, xenon and nitrogen were formed more rapidly indicating the formation of $Xe(N_3)_2$, but definitive proof for the existence of this compound was not possible. Attempts to trap the azide group from $Xe(N_3)_2$ with fluoroolefins were unsuccessful.

Another transfer agent sought was Me_3SiClO_3 from the reaction of Me_3SiCl and $KClO_3$. While the $KClO_3$ was apparently converted to KCl, Me_3SiF was observed rather than Me_3SiClO_3, possibly due to reaction of the formed silyl chlorate with fluoride passivation films on the metal vacuum system. An all glass system was used to reinvestigate this reaction but only a moderate conversion of the $KClO_3$ occurred and no Me_3SiClO_3 or other chlorine oxide was isolated.

Another transfer agent studied was nitryl azide. This compound was claimed to be generated from alkali metal azides and nitronium fluoroborate and to be stable in solution below -10C. Attempts to verify this synthesis were not successful. An alternative synthesis was tried using HN_3 and FNO_2 in anhydrous HF solution. This solution was found to be shock sensitive. Furthermore, an apparent equilibrium exists in HF between NO_2N_3 and NO_2HF_2. Thus reaction with a fluoroolefin gave equivalent yields of the FNO_2

adduct (from NO_2HF_2 reaction) and nitrous oxide (from NO_2N_3 decomposition). A novel, fast, simple technique was developed for the synthesis of FNO_2 from $NaNO_2$ and BrF_5 in high yield.

The final transfer agent examined was N_3SO_3F. We have studied its formation from sodium azide and peroxy disulfuryl difluoride. This reaction gave the expected decomposition products N_2 and $S_2O_5F_2$ but the other anticipated product, N_2O, was not observed.

The second area investigated was the synthesis of perfluorovinyl olefins substituted with energetic groups. One energetic group was SF_5O-. As a starting point the addition of SF_5OCl to three different unsymmetrical fluoroethylenes was carried out. These reactions gave the new compounds SF_5OCF_2CFHCl, $SF_5OCFClCF_2Cl$, and the isomer mixture $SF_5OCFBrCF_2Cl/SF_5OCF_2CFBrCl$ in 44-59% yield. In addition SF_5OF and CFCl=CFCl were also reacted to form the above dichloro derivative in 77% yield. All of these materials were characterized by spectroscopic and physico-chemical measurements. They exhibited excellent thermal and chemical stability. Numerous attempts were made to dehalogenate $SF_5OCFClCF_2Cl$ and also $SF_5OCFBrCF_2Cl$ in its isomer mixture in order to obtain $SF_5OCF=CF_2$. Zinc powder, zinc-copper couple, and triphenyl phosphine were examined as reductants in a variety of solvents and without solvent. When reaction occurred it resulted in the degradation of the SF_5O- group. No olefinic materials were obtained.

The second energetic group of interest in connection with the perfluorovinyl moiety was the nitro group. Approaches to the desired compound, $CF_2=CFNO_2$, involved perfluorovinyl metal organic reagents. Perfluorovinyl cadmium iodide was synthesized in DMF and was also converted to perfluorovinyl mercury chloride. Neither compound produced the desired $CF_2=CFNO_2$ when reacted with FNO_2. Instead the dimerization product, perfluorobutadiene was formed together with some $CF_2{=}CFH$ and $CF_3CFH(NO_2)$. Attack on the solvent by FNO_2 was noted via generation of significant amounts of CO_2 and N_2O. Perfluorovinyl cadmium iodide could not be synthesized in THF solvent and the alternate nitrating agent, NO_2BF_4, was not compatible with DMF.

FOREWORD

The research reported herein was supported by the U.S. Air Force Office of Scientific Research under Contract No. F49620-85-C-0037, with Dr. A. J. Matuszko as Scientific Officer. This report covers the period 1 March 1985 through 31 December 1986. Dr. C. J. Schack was the Program Engineer. The scientific effort was carried out by Drs. C. J. Schack and K. O. Christe assisted by Mr. R. D. Wilson in some of the SF_5O-chemistry. The program was administered originally by Dr. L. R. Grant and later by Dr. J. E. Flanagan.

CONTENTS

FIGURES

INTRODUCTION

This report covers a 22-month period and describes Rocketdyne's efforts in the area of energetic fluorocarbons with a goal of developing new reagents and syntheses for energetic highly fluorinated fluorocarbons. Areas to be studied include:

1. The synthesis and characterization of new transfer agents, XeY_2 and R_3SiY [$Y = N_3$, ClO_3, CF_2NO_2, $CF(NO_2)_2$], $B(N_3)_3$, N_3SO_3F, and NO_2N_3.

2. The use of these transfer agents in the preparation of novel energetic fluorocarbons by additions to unsaturated functions and displacements of reactive halogens from the fluorocarbon backbone.

3. The preparation of fluoroolefins containing energetic substituents such as N_3, NO_2, $CF(NO_2)_2$, and SF_5O, and conversion of these olefins to the corresponding epoxides.

4. Polymerization of the energetic fluoroepoxides to low molecular weight polyethers using procedures well known for the polymerization of related fluoroepoxides.

5. Investigation of the metal fluoride catalyzed nitration of fluorocarbon nitriles to produce fluorocarbon nitramines.

6. Interconversions of selected energetic substitutents on appropriate useful substrates employing known methods, eg. $R_fNO \rightarrow R_fN_3$ or R_fNF_2, $R_fN_3 \rightarrow R_fNF_2$, and $R_fOSO_2F \rightarrow R_fOF$, R_fCFO, R_fCO_2H.

These initial efforts have been concentrated on the synthesis of the new transfer agents and aspects of the chemistry of the SF_5O-substituted fluorocarbons.

DISCUSSION AND RESULTS

Presently employed composite propellant and explosive formulations are less than optimal owing to problems such as:

- nonenergetic binders
- insufficient thermal stability
- low density
- sensitivity/vulnerability

Significant performance improvements in these systems is possible through the use of more highly energetic binders. Unfortunately, the introduction of a large number of energetic groups into hydrocarbon-type binders usually reduces their stability. An obvious solution to this problem would be the use of energetic fluorocarbons. These compounds offer the advantages of high energy, high thermal stability, high density and usually also low sensitivity. Unfortunately, very little systematic work has been done in this area due to the generally low reactivity of fluorocarbons. As a consequence, the state-of-the-art in highly fluorinated binders is 3M's FC2202 (empirical formula $C_{2.88}H_{0.515}O_{2}F_{5.48}$) which is an hydroxyl terminated perfluoro polyether which does not contain any energetic groups. Its major drawback is its low energy content.

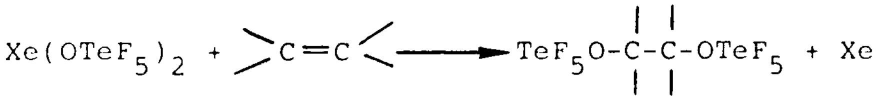
It should be pointed out that the performance of a perfluorinated binder can also depend on other factors, such as the hydrogen content of the system in which it is used. If, for example, the hydrogen content of the system is low, its performance is unimpressive. However, in hydrogen rich formulations, its performance is more attractive. This arises from the favorable thermodynamics for combustion to HF. At the same time sufficient oxygen is required to convert all the carbon to carbon monoxide. Regardless of the form in which nitrogen is present in a formulation, maximum performance is obtained when elemental nitrogen is the combustion product. Furthermore, it should be noted that in metallized formulations fluorine provides higher energy and combustion efficiency than oxygen through generation of volatile Al-F compounds. Together these requirements dictate that for practical application an energetic fluorocarbon should provide fluorine, oxygen and nitrogen formulated to yield HF, CO, and N_2 on combustion.

I. SYNTHESIS OF NOVEL TRANSFER AGENTS

Due to the generally encountered low reactivity of fluorocarbons, special highly active transfer agents are needed for the introduction of energetic groups into the fluorocarbon substrates. Our previous work and that of others has demonstrated that energetic side groups, such as N_3, NO_2, NF_2, ONF_2, and $OClO_3$, are generally as stable or more stable in fluorocarbons than they are in hydrocarbons. For the purpose of obtaining better methods for introducing the energetic groups into fluorocarbon molecules, our initial efforts were concerned with the synthesis of novel transfer agents.

A. Xenon Compounds

The chemistry of xenon compounds has shown continuous growth since the discovery of these compounds in 1962. A large part of this work has dealt with the use of XeF_2 to fluorinate organic substrates (Refs. 1,2). Either substitution or addition of fluorine to the substrate molecule occurs depending on the nature of the host and reaction conditions. More recently we have employed $Xe(OTeF_5)_2$ to transfer $OTeF_5$ groups to fluoroolefins and fluoroaromatics (Ref. 3).



$$Xe(OTeF_5)_2 + {>}C{=}C{<} \longrightarrow TeF_5O\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}OTeF_5 + Xe$$

These are high yield, easily moderated reactions. Based on the excellent results with these xenon transfer agents, the synthesis of the corresponding xenon azide, $Xe(N_3)_2$, was sought for its utilization in reactions with fluorocarbons.

XeF_2 was prepared by a modified literature method (Ref. 4). This entailed reaction of 2 parts xenon to 1 part fluorine under pressure at 400C for 2 hr. Excess xenon is required to suppress formation of higher valent xenon fluorides which might later react with active oxygen sources thereby contaminating the XeF_2 with the treacherously explosive XeO_3. Yields of XeF_2 were typically 95% on a 20 mmol scale and the unreacted xenon was recycled.

It is possible to envision the preparation of $Xe(N_3)_2$ according to the following equation:

$$XeF_2 + 2HN_3 \xrightarrow{\text{solv.}} Xe(N_3)_2 + 2HF$$

This method parallels those using $HOTeF_5$ (Ref. 5) and $HOSeF_5$ (Ref. 6) with XeF_2. Nevertheless, in view of the well known difficulties involved in working with hydrazoic acid, our initial attempts to synthesize $Xe(N_3)_2$ focused on the use of trimethyl silyl azide without solvent as the source of the azide group.

$$XeF_2 + 2Me_3SiN_3 \longrightarrow Xe(N_3)_2 + 2Me_3SiF$$

This silyl azide is a thermally very stable, low melting (-95C), soluble liquid (Ref. 7) and is commercially available. Formation of Me_3SiF would serve as an especially effective driving force for the reaction due to the high Si-F bond energy (135 kcal/mol). This impetus has been widely used in the chemistry of silyl compounds (Ref. 8).

Working on an approximately one mmol scale of XeF_2 and using Teflon-stainless steel ampoules it was found that a slow reaction occurred at -78 to -60C when liquid trimethyl silyl azide was placed onto the solid XeF_2 without any other solvent. Over the course of several days most of the projected by-product trimethyl silyl fluoride was observed as the most prominent among the volatile materials removable from the reactor by pumping at -78C (which did not remove unreacted trimethyl silyl azide). However the reaction was often very sluggish in generating Me_3SiF and when the temperature was raised above -60C to enhance the rate of reaction, other products became more prominent. These included non-condensable gas (presumably N_2), xenon, and HN_3.

The erratic rate of reaction was further illustrated by two virtually identical reactions conducted in stainless steel cylinders. These were planned as long term experiments at -60C. The first produced very little reaction at all in 19 days as evidenced by the small amount of Me_3SiF evolved, 13% of theoretical. However this was accompanied by Xe and N_2 equivalent to the decomposition of more than 53% of any formed $Xe(N_3)_2$. The second experiment after 12 days at -60C had resulted in consumption of the Me_3SiN_3 with generation of Me_3SiF, 97% of theoretical. Unfortunately $Xe(N_3)_2$ was not isolated but all the xenon and nitrogen expected from its decomposition were found. The variations in the reaction rate are attributed at least in part to differences in crystal size, and therefore surface area, of the XeF_2.

In order to promote efficient contact and to perhaps partially dissolve the XeF_2, CF_2Cl_2 was employed as a solvent in some reactions. These reactions were kept at various constant temperatures for 10 hrs. or more before monitoring for volatile by-products such as Xe, N_2, and Me_3SiF. At -60C or below practically no reaction occurred. At temperatures to about -40C the reaction was still slow but the formed Me_3SiF was consistently accompanied by Xe and nitrogen in quantities commensurate with the decomposition of the desired $Xe(N_3)_2$. At still higher temperatures the generation of these products accelerated as before.

Therefore it appears from the results that at <-60C, Me_3SiN_3 reacts with XeF_2 to generate $Xe(N_3)_2$ and Me_3SiF at a slow rate accompanied by a slower decomposition of the formed $Xe(N_3)_2$.

$$XeF_2 + 2Me_3SiN_3 \xrightarrow{<-60C} Xe(N_3)_2 + 2Me_3SiF \quad \text{slow}$$

$$Xe(N_3)_2 \xrightarrow{<-60C} Xe + 3N_2 \quad \text{slower}$$

However, above -60C, and especially above -40C, the decomposition reaction seems to become faster than the formation reaction. Measured Xe to N_2 ratios agreed well with the expected 1:3 stoichiometry. The small amounts of HN_3 consistently observed are thought to arise from hydrolysis of $Xe(N_3)_2$ in the Teflon FEP reactor or perhaps by the action of adventitious HF on Me_3SiN_3.

Two attempts were made to "trap" the azide radicals generated by $Xe(N_3)_2$ decomposition with fluoroolefins. These were hexafluoropropene and chlorotrifluoroethylene. The reactions were carried out by adding the olefin to the $Xe(N_3)_2$ reactor at low temperature and warming slowly to about -20C. In both cases the olefins were recovered unchanged.

From these results conclusive proof for the synthesis of $Xe(N_3)_2$ is not in hand but there are strong indications that it is generated below -60C and has low temperature and kinetic stability.

Improved synthetic procedures are necessary. It should be noted also that the observed by-product HN_3 evolved even in the presence of much unreacted XeF_2. It would therefore appear that the reaction of XeF_2 with HN_3 is not a promising synthetic route toward $Xe(N_3)_2$.

B. Silyl Compounds

Trialkyl silyl compounds are versatile carriers of ligands for many types of reactions (Refs. 8,9). Whereas XeY_2 reagents are useful in adding Y groups to double bonds, the R_3SiY reagents are useful in substitution reactions, particularly for the replacement of activated fluorine by Y. An as yet unknown trialkyl silyl transfer agent is Me_3SiClO_3. An attempt was made to prepare this compound by the following route:

$$Me_3SiCl + KClO_3 \longrightarrow Me_3SiClO_3 + KCl$$

Preliminary reactions carried out in stainless steel Teflon equipment were inconclusive due to reaction of Me_3SiCl with the fluoride passivation films normally present in our systems

$$Me_3SiCl + MF \longrightarrow Me_3SiF + MCl$$

An all glass and Teflon system was constructed. When this was used to analyze the reaction products the only new trimethyl silyl species observed was $Me_3SiOSiMe_3$. The reaction solution itself had become yellow colored probably due to the presence of Cl_2 and/or chlorine oxide decomposition products in the excess Me_3SiCl liquid. A possible sequence leading to these species is:

$$Me_3SiClO_3 \longrightarrow Me_3Si\dot{O} + ClO_2$$

$$Me_3Si\dot{O} + Me_3SiCl \longrightarrow Me_3SiOSiMe_3 + 1/2\ Cl_2$$

However, the formation of some of the observed $Me_3SiOSiMe_3$ by hydrolysis of Me_3SiCl cannot be excluded. In any case no evidence was found for Me_3SiClO_3.

C. Nitryl Azide

Nitryl azide is a novel energetic compound whose synthesis was claimed in 1973 (Ref. 10):

$$NO_2BF_4 + MN_3 \xrightarrow[<-10C]{solv.} NO_2N_3 + MBF_4$$

The product was not isolated and decomposed to nitrous oxide at OC. Solvents used were CH_3CN, $CHCl_3$, and CCl_4. Containing two dissimilar energetic groups in one molecule, this compound would provide a unique means of simultaneously introducing nitro and azido functions into suitable fluorocarbon substrates.

For our work on the preparation of NO_2N_3, commercial lithium or sodium azide were used together with NO_2BF_4 which was prepared at Rocketdyne. The identity and purity of these materials was verified by infrared spectroscopy (Ref. 11). Following closely the procedure described, and using Photrex grade acetonitrile which was protected from moisture by storage over 4A molecular sieves in the dry nitrogen atmosphere of the glove box, we attempted to duplicate the results reported. Complete dissolution of the reagents occurred. The MN_3 solution was cooled to -20 to -25C and the NO_2BF_4 solution was added slowly to it with stirring. No evidence was obtained for a precipitate, expected for the by-product MBF_4, at the temperatures studied or even when the concentration of the reagents was increased fivefold. The literature method was used to test for the presence of NO_2N_3 in the solution. The solution was allowed to warm toward ambient temperature and above OC slow gas evolution occurred. After this had ceased the gas condensable at -196C was separated and purified by fractional condensation. This gas was shown to be nitrous oxide by infrared spectroscopy (Refs. 11,12). However the amount obtained was always in the range of 30-45% of that expected for the reported decomposition scheme (Ref. 10) even with degassing of the solvent.

$$NO_2^+ + N_3^- \longrightarrow NO_2N_3 \longrightarrow 2N_2O$$

Nitrous oxide was stated to be the only gaseous product and to be evolved quantitatively. Obviously this did not happen. Perhaps nitrogen also evolved but this would not have been detectable since the reaction was run under dry air. These discrepancies discouraged any further efforts to prepare nitryl azide by this method.

An alternative procedure was investigated and it entailed the generation of HN_3 in excess anhydrous HF (Ref. 13) as a first step.

$$NaN_3 + HF \xrightarrow{HF} NaF + HN_3$$

The reaction was run at -78C and the HN_3/HF volatile material was then distilled into another trap at -78C while warming the reactor.

The second reactant required was nitryl fluoride. This was prepared by a previously unreported reaction using excess sodium nitrite and bromine pentafluoride according to the following stoichiometry.

$$5NaNO_2 + 2BrF_5 \longrightarrow 5NaF + 5FNO_2 + Br_2$$

The synthesis was conducted by condensing the BrF_5 into a cylinder containing the $NaNO_2$ at -196C and allowing the cylinder to warm up to ambient temperature for 2 hr. Vacuum fractionation through U-traps cooled to -142 and -196C gave pure FNO_2 in the low temperature trap as shown by infrared spectroscopy (Refs. 11,14). The yield of purified FNO_2 was 84% (5.30 mmol from 2.54 mmol BrF_5). The product may not be stored in the synthesis reactor since it degrades to NO_2 and other products. The procedure described represents a fast and simple route to FNO_2 and is a good alternative to the usual elemental fluorine reaction with nitrite (Ref. 15).

To the solution of HN_3 in HF at -78C was added a slight excess of freshly fractionated FNO_2.

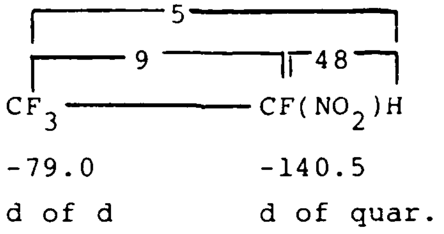
$$HN_3 + FNO_2 \xrightarrow{HF} NO_2N_3 + HF$$

On warming to -45C no evidence of instability was noted. Further warming to first -15C and then ambient temperature resulted in the gradual evolution of nitrous oxide. This amounted to 43% of that expected for NO_2N_3 decomposing exclusively to N_2O. Some noncondensable gas also evolved which most likely was nitrogen. A second preparation was carried out but while adding dry ice to the storage dewar this product exploded. Thus either the NO_2N_3 or perhaps HN_3 in equilibrium with it, was clearly shown to be shock sensitive. This of course was not unexpected.

A third preparation of NO_2N_3 was carried out using HN_3 and FNO_2 in HF. In order to trap the nitryl azide this solution was treated with trifluoroethylene at -78C for 1.5 days before slowly warming over a day to room temperature with periodic monitoring of the volatile products. Together with unreacted trifluoroethylene and HF there was obtained a 43% yield of N_2O together with a 48 yield of the nitrofluorocarbon CF_3CFHNO_2. No azido fluorocarbon was detected. These results indicate that an equilibrium may exist as shown below:

$$NO_2{}^+N_3{}^- \xrightleftharpoons{HF} NO_2{}^+HF_2{}^- + HN_3$$

The nitryl azide decomposes at elevated temperature in the normal fashion to give N_2O while the nitronium bifluoride acts as a nitrofluorinating agent for the olefin. The effective addition of FNO_2 to this fluoroolefin is known (Ref. 16) from a different reagent system, HNO_3 + HF. Figure 1 shows the infrared spectrum of this nitrofluorocarbon. Noteworthy are the strong bands at 1610 and 1280 cm^{-1} attributable to $\nu_{as}NO_2$ and $\nu_{s}NO_2$ respectively. The ^{19}F nmr spectrum agreed with the formulation as $CF_3CFH(NO_2)$.



The failure of NO_2N_3 to add to the olefin may well be attributed to the high acidity of HF. Further work with NO_2N_3 in this regard would require the use of different, less acidic solvent systems.

D. Trinitrogen Fluorosulfate

The final transfer agent investigated was trinitrogen fluorosulfate, N_3SO_3F, whose synthesis was explored using the following route.

$$NaN_3 + FO_2SOOSO_2F \longrightarrow NaSO_3F + N_3SO_3F$$

Exposure of sodium azide to the peroxide at OC to room temperature led to the formation of sodium fluorosulfate and the expected decomposition products, N_2 and $S_2O_5F_2$, but N_2O, a weak infrared absorber, was not observed. A scheme accounting for these products is:

$$[N_3OSO_2F] \longrightarrow N_2 + [\cdot NOSO_2F] \longrightarrow 1/2\ N_2O + 1/2\ S_2O_5F_2$$

No new stable trinitrogen species were obtained.

II. SYNTHESIS OF ENERGETIC MONOMERS

For energetic binders the most desirable type of polymeric chain is a polyether due to its good thermal stability, flexibility, glass transition point, and load bearing capability. The desired polyethers are obtained by polymerization of epoxide monomers, which in turn are prepared by epoxidation of olefins. Consequently the synthesis of energetic monomers for binder applications should involve the synthesis of suitable olefins such as $CF_2=CFY$, where Y is an energetic group such as NO_2, N_3, or SF_5O.

A. SF_5O Compounds

The first energetic group examined was SF_5O- which when substituted into fluorocarbons not only adds to the density (Ref. 3) but the relatively weak S-F bonds (77 kcal/mol compared to 67 kcal/mol in NF_2) and high oxidation state (+VI) of sulfur make it an energetic oxidizing substituent. Consideration of SF_5- groups in this context has been reported (Ref. 17) and has led to a compilation of properties of various known SF_5- compounds (Ref. 18). In addition the SF_5O- group possesses excellent stability in fluorocarbons (Ref. 19).

The commercially non-available inorganic sulfur precursors, SOF_4, SF_5OCl, and SF_5OF were synthesized by established procedures (Refs. 20,21).

$$SOCl_2 + 2NaF \longrightarrow SOF_2 + 2NaCl$$

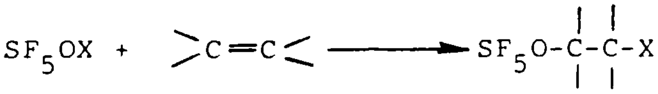
$$SOF_2 + F_2 \longrightarrow SOF_4$$

$$SOF_4 + ClF \xrightarrow{CsF} SF_5OCl$$

$$SOF_4 + F_2 \xrightarrow{CsF} SF_5OF$$

Typical yields are greater than 90% in each of these steps.

While SF_5OX additions to olefins, where X=Cl or F, have been known for some time (Refs. 19,22-24) these reactions have been limited to symmetrical fluoroolefins or non-fluorinated olefins. With care, all of these reactions produced acceptable yields of the corresponding 1:1 adducts through cleavage of the OX bond.



$$SF_5OX + >C=C< \longrightarrow SF_5O-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X$$

However, no examples have been reported for unsymmetrical highly fluorinated olefins, in particular those that might furnish suitable products for subsequent conversion to the unknown perfluorovinyl derivative, $SF_5OCF=CF_2$.

Accordingly reactions of SF_5OX and highly fluorinated olefins were carried out as shown by the equations:

$SF_5OCl + CF_2=CFH \longrightarrow SF_5OCF_2CFHCl$ 44% yield

$SF_5OCl + CF_2=CFCl \longrightarrow SF_5OCFClCF_2Cl$ 50%

$SF_5OF + ClCF=CFCl \longrightarrow SF_5OCFClCF_2Cl$ 77%

$SF_5OCl + CF_2=CFBr \longrightarrow SF_5OCFBrCF_2Cl + SF_5OCF_2CFBrCl$ 59%

77% + 23% isomer mixture

These reactions required careful control. For example when $CF_2=CFBr$ was added fairly rapidly to SF_5OCl at -78C, the yield of SF_5OR_f fell significantly. The principal by-products were SF_4O and chloro-fluorinated adducts. All of the SF_5O-substituted fluorocarbons are thermally stable, storable, clear, colorless liquids of moderate volatility.

The observed modes of addition for SF_5OCl are in general agreement with an electrophilic chlorine attacking the olefins as described for the analogous reactions of CF_3OCl (Ref. 25). However the finding of one isomeric adduct only in the case of $CF_2=CFCl$ was surprising since both the above mentioned CF_3OCl (Refs. 19,24) and FO_2SOCl (Ref. 26) gave both isomers. No simple explanation is apparent for this difference. Additional data concerning these new SF_5O- species are given in the Appendix and their infrared spectra are shown in Figs. 2-4.

Since trifluoroethylene did not provide the $SF_5OCFHCF_2Cl$ isomer sought for subsequent dehydrohalogenation, the formed isomer was not studied further. However, since both the chloro and bromo ethylenes gave exclusively or mainly an adduct suitable for dehalogenation, the following reactions were attempted.

$$SF_5OCFClCF_2Cl \xrightarrow{M} SF_5OCF=CF_2 + MCl_2$$

$$SF_5OCFBrCF_2Cl \xrightarrow{M} SF_5OCF=CF_2 + MBrCl$$

Nineteen separate attempts were made to accomplish this dehalogenation using one or the other of the above olefins. These experiments included:

- Zinc powder unactivated or activated by literature procedure (Ref. 27) and Zn powder from different sources.
- Trifluoroacetic acid or $ZnCl_2$ catalysis.
- Zinc-Copper couple powder.
- Temperatures from 45 to 195C for from 1-72 hr.
- The solvents dimethyl sulfoxide, dioxane, dimethyl formamide, and diglyme; all dried carefully.
- No solvent.
- Reactions vessels of all glass construction or stainless steel cylinders.
- Ultrasound activation.

In these experiments it was observed that most of the R_fOSF_5 starting compound could be recovered below 100C in the case of the dichloro compound but less in the case of the bromo chloro compound. In the absence of a solvent these compounds were only slightly decomposed after days at 195C in stainless steel. No olefin products were observed in any of these reactions. Degradation of the R_fOSF_5 compound was indicated by the finding of SO_2F_2 and SOF_2 accompanied by various fluoroacyl halides, fluoroalkyl halides, and solvent derived products such as CH_3F.

One final attempt to dehalogenate $SF_5OCFBrCF_2Cl$ was carried out using triphenylphosphine as the reactive agent based on its reported superiority to Zn in some fluorocarbon chloride dechlorinations (Ref. 28). Using the same conditions and solvent, dioxane, no interaction was noted in 2 hr at 40-75C nor several days at room temperature and no fluoroolefin was isolated.

The fact that all of these systems failed was surprising. Some difficulty had been anticipated since dehalogenation of $CF_3OCFClCF_2Cl$ with Zn to give $CF_3OCF{=}CF_2$ has been described (Ref. 29) to occur to a significant extent only in dimethyl sulfoxide among several solvents tested. Also the corresponding SF_5- olefin derivative, $SF_5CF{=}CF_2$, is well known but it is obtained by a dehydrohalogenation path (Refs. 30,31).

$$SF_5CFHCF_2X \xrightarrow[-HX]{KOH} SF_5CF{=}CF_2 \qquad (X{=}Br,\ Cl)$$

It is not apparent why the SF_5O- group so thoroughly inhibits the dehalogenation reaction.

No further attempts were made to prepare $SF_5OCF{=}CF_2$ via dehalogenation processes.

B. Nitrotrifluoroethylene

The second energetic group of interest in connection with the perfluorovinyl moiety was the nitro group. Approaches to this unknown, but desired, compound, $CF_2{=}CFNO_2$, involved metal organic reagents. The low thermal stability of fluorocarbon lithium and Grignard reagents has limited their synthetic utility (Ref. 32). Recently, Burton and coworkers (Refs. 33,34) have demonstrated that the readily formed cadmium derivatives of a number of perfluoroalkenyl halides have excellent thermal stability coupled with excellent reactivity in a number of applications including stereospecific syntheses. The general synthetic reaction is shown for the vinyl case.

$$CF_2{=}CFI + Cd \xrightarrow{\text{RT-60C}} CF_2{=}CFCdI + (CF_2{=}CF)_2Cd + CdI_2$$

The mono to bis ratio obtained varies with the alkene but both cadmium reagents exhibit the same reaction chemistry. Various solvents have been employed in these organo metal syntheses.

Since the cadmium reagents are known to readily exchange their fluorovinyl ligand for a strongly polarized halogen, the reaction of the perfluorovinyl cadmium reagents with FNO_2 was explored as a route to $CF_2{=}CFNO_2$:

$$(CF_2{=}CF)CdX + \overset{\delta^-\delta^+}{FNO_2} \longrightarrow CF_2{=}CFNO_2 + FCdX$$

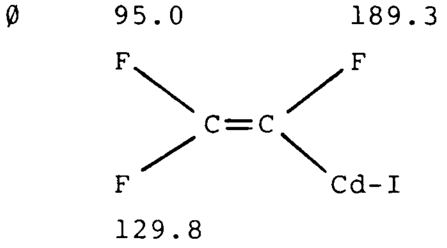
The cadmium powder employed for the synthesis of $(CF_2{=}CF)CdX$ was activated by washing for one min. in 3% HCl (4 times), water (5 times), absolute methanol (4 times), and ether (2 times); decanting being used to remove the washings (Ref. 35). Following this the powder was dried under vacuum and stored and weighed out in the dry nitrogen atmosphere of the glove box. Solvents were anhydrous, spectrophotometric grade and were stored over molecular sieves (Ref. 36).

Initially we had selected tetrahydrofuran as the solvent to use because of its volatility and relative inertness. It had been successfully used by Burton in perfluoroalkenyl-zinc systems (Ref. 34). Despite much careful effort it was found that this solvent was unsuitable for the vinyl-cadmium system. Reaction could not be obtained. In order to verify that the THF was not in some way contaminated, the previously reported reaction with perfluoro-n-propyl iodide and cadmium was carried out in the THF. This proceeded smoothly at 45-50C and was complete in one hour. Analysis of the solution by ^{19}F nmr showed no unreacted n-C_3F_7I but a mixture of 92.5 mole % n-C_3F_7-Cd-I and 7.5% (n-$C_3F_7)_2Cd$.

	CF_3—	CF_2—	CF_2—CdI	(CF_3—	CF_2—	$CF_2)_2Cd$
φ	82.5	132.8	138.6	81.3	120.6	126.7
multiplicity	trip.	quart.	d of mult.	trip.	quart.	sing.

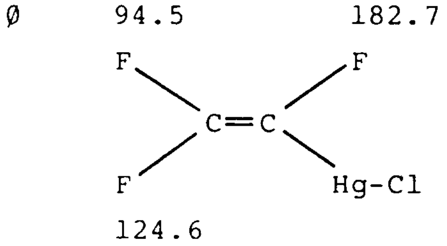
These values agreed well with similar data reported by Naumann for diglyme solutions (Ref. 37). Therefore it was shown that THF while useful for some organometallic syntheses is not applicable for the specific case of perfluorovinyl cadmium reagents.

Accordingly we switched to the proven, alternate solvent dimethylformamide. With DMF a typical reaction consisted of loading oven dried glassware with Cd powder (10 mmol) and solvent in the glove box. Under dry nitrogen and stirring, CF_2=CFI (11-12 mmol) was added dropwise over a few minutes. Reaction occurred at once and was continued by heating at approximately 50C for 2-3 hr. After recooling to room temperature this black solution was filtered under pressurized nitrogen. The ^{19}F nmr spectrum of the filtrate showed the presence of 69% CF_2=CFCdI and 31% unreacted CF_2=CFI.



J gem - 108 Hz
cis - 45
trans - 108
doub. of doub.

When $HgCl_2$ was added to the filtrate transmetallation occurred to form the vinyl mercury derivative, CF_2-CFHgCl.



J gem - 85 Hz
cis - 42
trans - 116
doub. of doub.

These nmr values are comparable to those reported for $(CF_2=CF)_2Hg$ (Ref. 38). Iodo trifluoroethylene was unaffected by the $HgCl_2$.

A portion of the vinyl cadmium solution was transferred in the glove box to a Teflon U-trap containing a stirring bar. When attached to the vacuum line this trap was cooled, evacuated, and rewarmed. Freshly fractionated FNO_2 was then bled into the trap building pressure to about 0.5 atmosphere or higher while stirring the solution. Only a slight pressure drop occurred over several hours at ambient temperature. However, on work up via fractional condensation it was determined that much of the FNO_2 had been consumed. Among the volatile products separated from the solution at -45C were CF_2=CFH and $CF_3CFH(NO_2)$ comprising a few per cent of the fluorocarbons produced together with about a 25-50% yield of CF_2=CFCF=CF_2

(Ref. 39), based on the Cd reagent, as well as unreacted CF_2=CFI originally present in the mixture. Inorganic species observed as volatile compounds were CO_2, N_2O and NO_2 together with non-condensable gases, presumably N_2 and/or O_2. The always significant amounts of CO_2 and N_2O are attributable to attack of the FNO_2 on the solvent DMF. Examination of the reaction solution by nmr revealed that none of the vinyl cadmium reagent remained although some CF_2=CFI was still present.

These results are consistent with the following path.

$$CF_2{=}CFCdI + FNO_2 \longrightarrow CF_2{=}\dot{C}F + CdFI + \dot{N}O_2$$

$$2CF_2 = \dot{C}F \longrightarrow CF_2{=}CFCF{=}CF_2$$

Protic acid species from the solvent $-FNO_2$ reaction or traces of water would react as shown.

$$CF_2{=}CFCdI + H^+ \longrightarrow CF_2{=}CFH + CdI^+$$

$$CF_2{=}CFH + FNO_2 \longrightarrow CF_3CFH(NO_2)$$

The last step has already been discussed earlier in this report.

In order to moderate the course of the reaction and minimize the dimerization, a reaction temperature of -30C was used. This resulted in more uptake of FNO_2 as measured by pressure decrease of the FNO_2 ullage gas. Unfortunately the products were unchanged. Thus the reaction of CF_2=CFCdI and FNO_2 in DMF is not a viable route to $CF_2=CFNO_2$. Another source of NO_2 was considered, i.e. NO_2BF_4. However it was found that this salt and DMF are incompatible.

A different scheme for the formation of $CF_2{=}CFNO_2$ was the following reaction.

$$CF_2{=}CF_2 + NaNO_2 \xrightarrow{DMF} NaF + CF_2{=}CFNO_2$$

After 3 weeks stirring at ambient temperature it was found that most of the perfluoroethylene was recoverable but some attack on the solvent had occurred yielding CO_2, N_2O, and NO_2. Thus again we were not able to prepare $CF_2{=}CFNO_2$.

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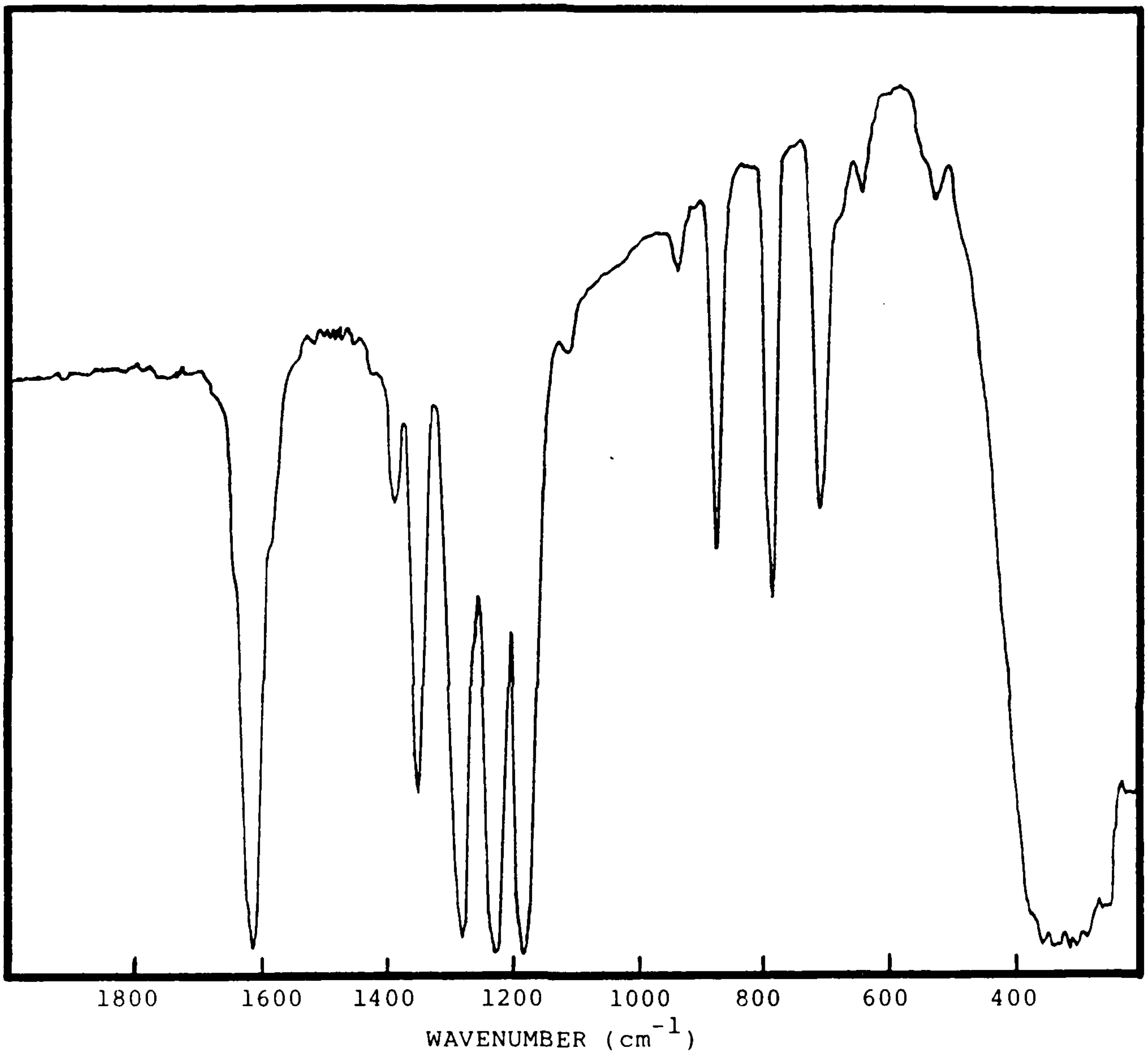

Fig. 1. $CF_3CFH(NO_2)$ (gas, 20mm) (AgCl windows)

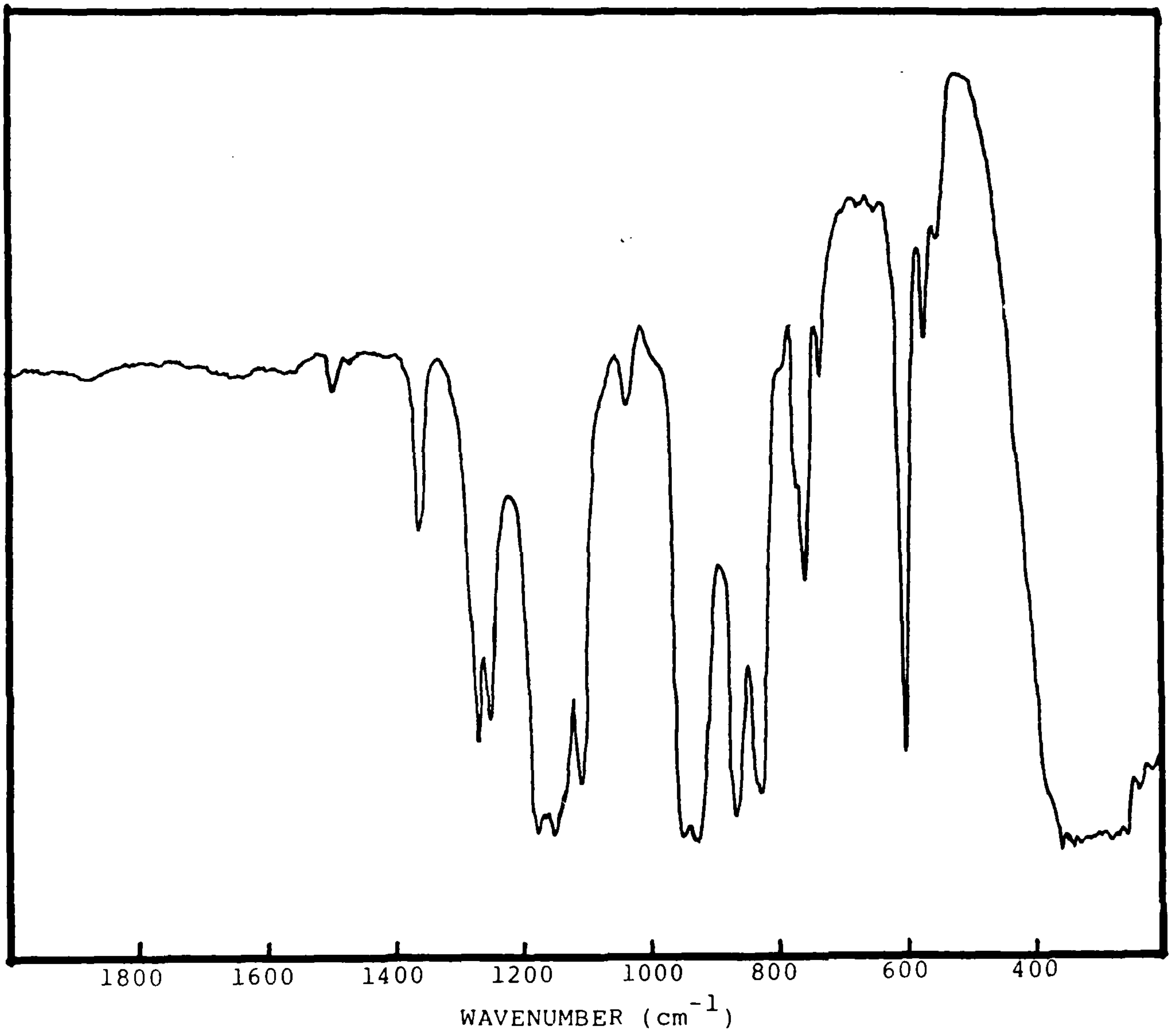

Fig. 2. SF_5OCF_2CFHCl (gas, 15mm) (AgCl windows)

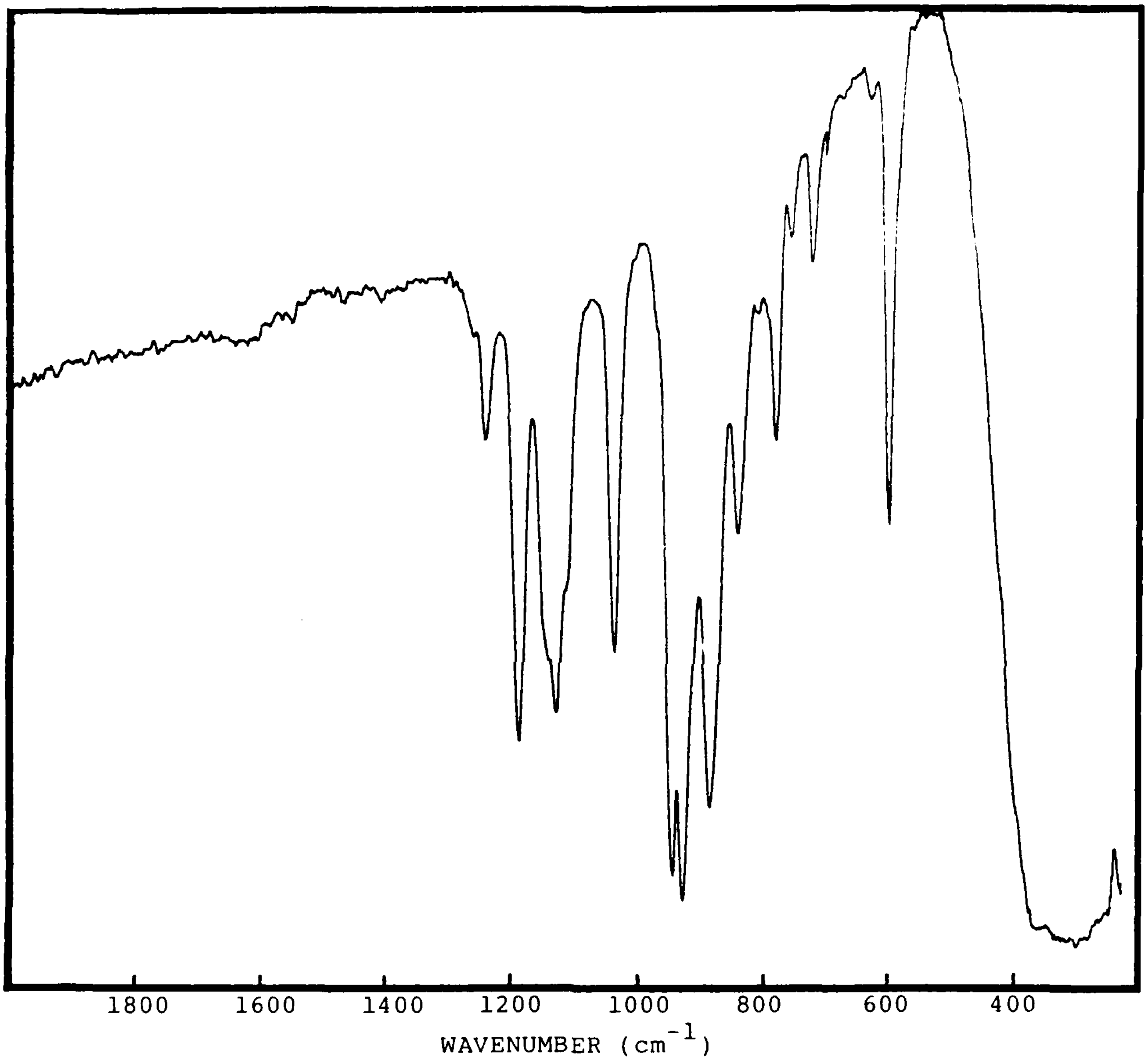

Fig. 3. $SF_5OCFClCF_2Cl$ (gas, 4mm) (AgCl windows)

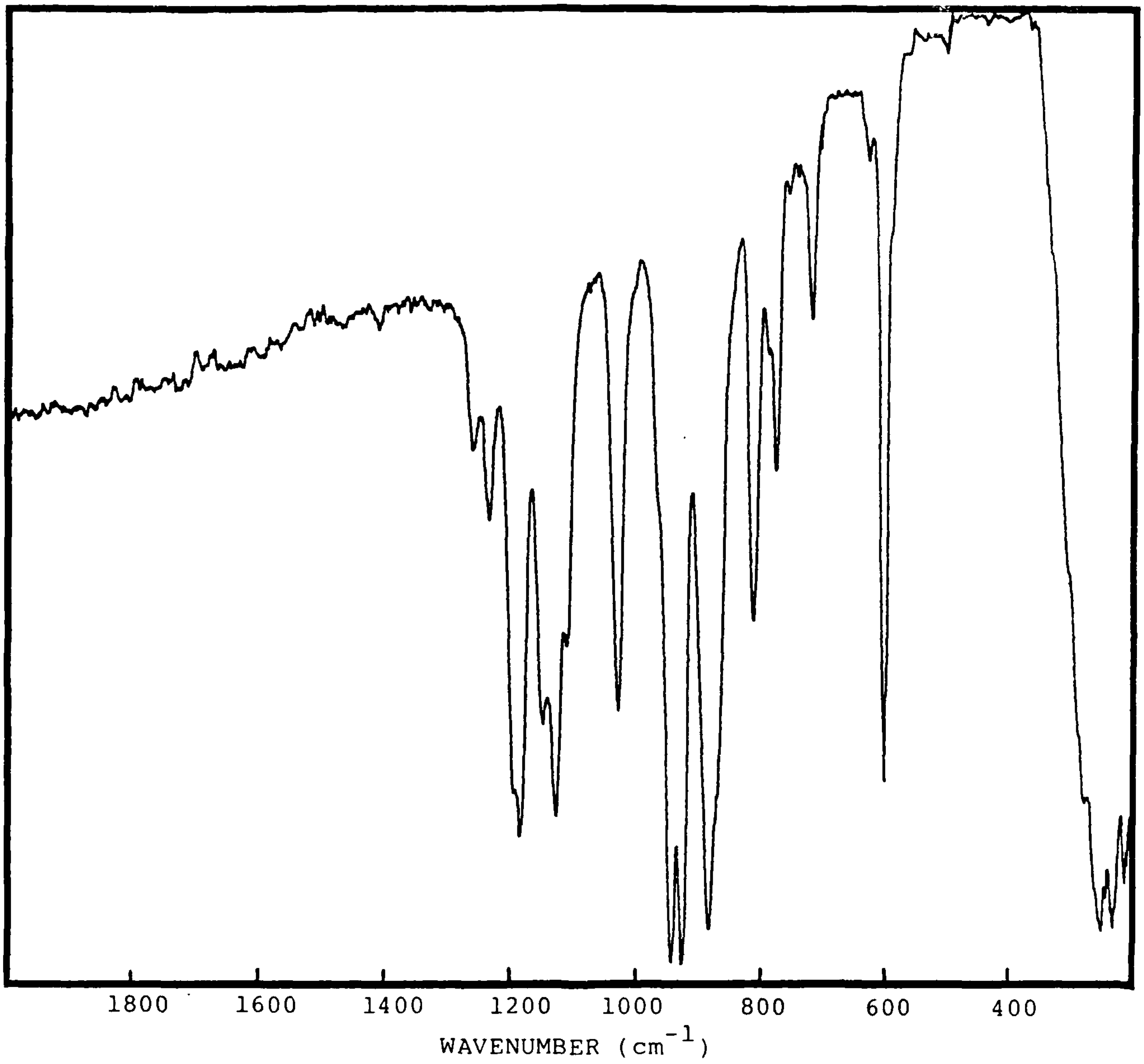

Fig. 4. $SF_5OCFBrCF_2Cl/SF_5OCF_2CFBrCl$ (gas, 3mm) (AgBr windows)

STATUS OF THE RESEARCH EFFORT

Reactions in CF_2Cl_2 solvent and solvent free reactions of solid xenon difluoride and liquid trimethyl silyl azide at low temperatures gave trimethyl silyl fluoride, the expected by-product from the formation of the unknown $Xe(N_3)_2$. Further indications of the presence of $Xe(N_3)_2$ was the generation of Xe and N_2 in approximately 1:3 ratio at temperatures above -60C.

Attempts to trap the azide group from $Xe(N_3)_2$ before or during its decomposition were unsuccessful.

Trimethyl silyl chloride and potassium chlorate reacted to form KCl but the coproduct Me_3SiClO_3 was not isolated. It decomposed to $Me_3SiOSiMe_3$ and Cl_2/ClO_x in glass or reacted with surface metal fluoride in metal systems to form Me_3SiF.

The claimed synthesis of nitryl azide was investigated using alkali metal azides and nitronium fluoroborate in acetonitrile. We were unable to verify the formation of this compound.

An alternate method of preparing nitryl azide from hydrazoic acid and nitryl fluoride in anhydrous hydrogen fluoride was investigated. An equlibrium involving NO_2N_3 and NO_2HF_2 was indicated in this solvent. Reaction with trifluoroethylene gave N_2O and $CF_3CFH(NO_2)$ in amounts indicating nearly equivalent concentrations of NO_2N_3 and NO_2HF_2 in the solution. This solution is shock sensitive.

A novel, fast, simple method was developed for synthesizing nitryl fluoride from sodium nitrite and bromine pentafluoride.

The synthesis of the unknown trinitrogen fluorosulfate was examined via sodium azide and peroxydisulfuryl difluoride. Only the decomposition products nitrogen and $S_2O_5F_2$ were isolated.

Addition reactions of SF_5OCl and unsymmetrical fluoroethylenes were carried out to furnish new SF_5O- substituted fluorocarbons. An alternate route to one of these new SF_5OR_f compounds using SF_5OF and a chlorofluoroethylene was also found and proceeded in higher yield. All of these compounds were thoroughly characterized.

Numerous attempts to dehalogenate the SF_5O- substituted fluorocarbons in order to prepare $SF_5OCF=CF_2$ were unsuccessful using conventional and uncommon techniques. Either no reaction occurred or the SF_5O- group was degraded.

Preparations of the vinyl cadmium reagent $CF_2=CFCdI$ and $(CF_2=CF)_2Cd$ were carried out in DMF but could not be effected in THF. The latter solvent was, however, useful in preparing n-C_3F_7CdI.

Efforts to synthesize $CF_2=CFNO_2$ from the vinyl cadmium reagent using FNO_2 resulted primarily in the formation of $CF_2=CFCF=CF_2$ and a lesser amount of $CF_2=CFH$ and $CF_3CFH(NO_2)$. Attack on the solvent gave CO_2, N_2O, and NO_2 products. No evidence for $CF_2=CFNO_2$ was obtained.

Displacement of fluoride from tetrafluoroethylene to give $CF_2=CFNO_2$ using $NaNO_2$ in DMF in a long term reaction gave only solvent related degradation products.

Transmetallation of the vinyl cadmium reagent to $CF_2=CFHgCl$ was accomplished using $HgCl_2$.

PUBLICATIONS

"Chlorine Fluoride," by C. J. Schack and R. D. Wilson, Inorganic Syntheses," 24, 1 (1986).

"Sulfur Chloride Pentafluoride," by C. J. Schack, R. D. Wilson, and M. W. Warner, Inorganic Syntheses, 24, 8 (1986).

"Chlorine Fluorosulfate," by C. J. Schack and R. D. Wilson, Inorganic Syntheses, 24, 6 (1986).

"Reactions of TeF_5OCl with Fluorocarbon Iodides," by C. J. Schack and K. O. Christe, J. Fluorine Chem., in press.

"Pentafluorotelluriumoxide Derivatives of Fluorocarbons," by C. J. Schack and K. O. Christe, to be published in J. Fluorine Chem.

"Synthesis of Pentafluoroseleniumoxide Fluorocarbons," by C. J. Schack and K. O Christe, to be published in J. Fluorine Chem.

"Synthesis of SF_5O- Substituted Fluorocarbons," by C. J. Schack, R. D. Wilson and K. O. Christe, to be published in J. Fluorine Chem.

PERSONNEL

Dr. C. J. Schack has been the principal investigator on this program. Valuable contributions, especially on spectroscopic matters, have been furnished by Dr. K. O. Christe. Dr. Christe was the recipient recently of the Fluorine Division of the American Chemical Society's Award for Creative Work in Fluorine Chemistry. Mr. R. D. Wilson assisted in some of the SF_5OR_f work and Dr. L. R. Grant has provided helpful discussions and guidance.

INTERACTIONS

PAPERS

A paper entitled "TeF_5O- Derivatives of Fluorocarbons" was presented at the Seventh Winter Fluorine Conference on Fluorine Chemistry in February 1985. In addition a session of the conference was chaired.

A paper entitled "Energetic Fluorocarbons" was presented at the AFOSR/AFRPL Rocket research Meeting in March 1985.

A paper entitled "TeF_5O- and SeF_5O- Substituted Fluorocarbons" was presented at an invited seminar at the University of California, Santa Barbara in March 1985.

A paper entitled "Synthesis of Pentafluoroseleniumoxide Fluorocarbons" was presented at the American Chemical Society National Meeting in April 1986.

A paper entitled "Synthesis of SF_5O- Substituted Fluorocarbons and Comparison to Some SeF_5O- and TeF_5O- Analogs" was presented at the International Symposium on the Centenary of the Discovery of Fluorine, Paris, August 1986.

CONSULTATION

Advice, consultation, and experimental testing were provided to the Science Center of Rockwell International regarding the synthesis of conductive organic films. In addition the synthesis of non-commercially available alkyl substituted pyrroles was carried out for that organization. These efforts were in support of Air Force programs at the Science Center dealing with doped films as non-metallic conductors and energy absorbers.

Advice and consultation was provided to the Rocketdyne Laser Organization concerning the safe handling of HNCO for use as a potential laser reactant in Air Force laser systems.

Commercial n-C_3F_7I was purified for use by the Rocketdyne Laser Organization as a fuel on an Air Force laser program.

Analytical procedures were improved for tetrafluorohydrazine. The N_2F_4 is employed at Rocketdyne as a reactant in the preparation of a propellant binder for use on an Air Force propellant program.

PATENTS

ISSUED

"Pentafluorotelluriumoxide Fluorocarbons," C. J. Schack and K. O. Christe, U.S. 4,508,662 April 2, 1985.

"Alkyl, Azido, Nitro Ethers and Method of Preparation," C. J. Schack and J. E. Flanagan, U.S. 4,522,756 June 11, 1985.

"Process for Preparing Pentafluorotellurium Hypofluorite," C. J. Schack and K. O. Christe, U.S. 4,594,232 June 10, 1986.

APPLIED FOR

"Multi(TeF_5O)- Substituted Fluorocarbons," C. J. Schack and K. O. Christe.

"Oxidation of Fluorocarbon Iodides with Pentafluorotellurium Hypochlorite and Derivatives Thereof," C. J. Schack and K. O. Christe.

"Synthesis of R_fOTeF_5," C. J. Schack and K. O. Christe.

DISCOSURES SUBMITTED

"Pentafluoroseleniumoxide Fluorocarbons," C. J. Schack and K. O. Christe.

APPENDIX

SYNTHESIS OF SF_5O- SUBSTITUTED FLUOROCARBONS

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SUMMARY

The reactions of SF_5OCl and SF_5OF with fluorinated ethylenes were used to prepare new SF_5O- substituted fluorocarbons in 44-77% yield. Compounds prepared were SF_5OCF_2CFHCl, $SF_5OCFClCF_2Cl$, and the isomeric mixture $SF_5OCFBrCF_2Cl/SF_5OCF_2CFBrCl$. Spectroscopic and other characterizing data for the adducts are presented. Numerous attempts to prepare $SF_5OCF{=}CF_2$ by dehalogenation of the dichloro or bromochloro materials were unsuccessful.

INTRODUCTION

While SF_5OX additions to olefins, where X=Cl or F, have been known for some time [1-4], these reactions have been limited to symmetrical fluoroolefins or non-fluorinated olefins. With care, all of these reactions produced acceptable yields of the corresponding 1:1 adducts through cleavage of the OX bond.

$$SF_5OX + \mathord{>}C{=}C\mathord{<} \longrightarrow SF_5O-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X$$

However, no examples have been reported for unsymmetrical highly fluorinated olefins, in particular those that might furnish suitable products for subsequent conversion to the unknown perfluorovinyl derivative, $SF_5OCF{=}CF_2$. It was of interest therefore to examine such additions involving SF_5OX compounds.

EXPERIMENTAL

Volatile materials were manipulated in a stainless steel vacuum line equipped with Teflon FEP U-traps, 316 stainless steel bellows-seal valves, and a Heise Bourdon tube-type gauge. The synthetic reactions employed here were conducted in stainless steel cylinders or a U-trap on the vacuum line. Infrared spectra were recorded on a Perkin Elmer Model 283 spectrophotometer using cells equipped with AgCl or AgBr windows. Raman spectra were recorded at ambient temperature on a Cary Model 83 spectrophotometer with the use of the 488-nm exciting line of an Ar ion laser. Sealed 3mm OD Quartz tubes were used as sample containers. ^{19}F NMR spectra were recorded at 84.6 MHz on a Varian Model EM390 spectrometer with internal $CFCl_3$ as a standard with a negative chemical shift being upfield from $CFCl_3$. Literature methods were used to prepare SF_5OCl [5] and SF_5OF [6]. Olefins used were commercial products (SCM Specialty Chemicals).

Reaction of SF_5OCl with CF_2=CFH.

A prepassivated, evacuated cylinder was cooled to -196°C and loaded successively with SF_5OCl (3.95 mmol) and CF_2=CFH (4.51 mmol) from the vacuum line. The cylinder was kept at -60°C for 20 hr. Fractional condensation of the products was carried out using a series of traps cooled at -64, -78, and -196°C. The olefin adduct was retained in the trap at -78°C (1.74 mmol, 44% yield). Identification of the adduct as SF_5OCF_2CFHCl was based on its ^{19}F and ^{1}H nmr spectra together with infrared, and Raman spectra. Vapor density; Found 258, calc. 260 g/mol. Vapor pressure-temperature data recorded were (T°C; P, mm): -31.7, 11; -24.5, 16; 0.0, 47; 9.8, 70; 23.1, 108. For the range -32 to 23°C $\log P_{mm} = 6.4314 - 1300.4/T°K$ with a calc. b.p. = 93°C and ΔH_v = 5.95 kcal/mol.

Reaction of SF_5OCl with CF_2=CFCl.

Sequential additions of SF_5OCl (6.23 mmol) and CF_2=CFCl (6.86 mmol) were made to a passivated, cold (-196°C) 30 ml stainless steel cylinder attached to the vacuum line. The closed cylinder was then left at -60°C overnight before warming to -20°C for 2 hrs. Fractional condensation of the products in a series of traps cooled to -56, -64 and -196°C resulted in retention of the SF_5O- adduct in the trap cooled to -64°C (3.09 mmol, 50% yield). This adduct was identified as $SF_5OCFClCF_2Cl$ on the basis of its ^{19}F nmr, infrared, and Raman spectra. Vapor density; Found, 292, calc. 295 g/mol. Vapor pressure-temperature data recorded were (T°C, P_{mm}): -31.9, 7; -23.4, 11; 0.0, 35; 19.5, 78. For the range -32 to 20°C log P_{mm} = 6.8252-1443.4/T°K with a calc. b.p. 93°C and ΔH_v = 6.60 kcal/mol.

Reaction of SF_5OCl with CF_2=CFBr.

A 10.5 mmol sample of SF_5OCl was maintained at -78°C in a U-trap on the vacuum line and CF_2=CFBr (11.0 mmol) was bled into the trap slowly over 3 hr before the contents were warmed toward room temperature. Separation of the products were carried out by fractional condensation in U-traps cooled, to -31, -78, and -196°C. The desired adduct was retained in the -78°C trap (6.16 mmol, 59% yield) and was identified as a mixture of the isomers $SF_5OCFBrCF_2Cl$ and $SF_5OCF_2CFBrCl$ based on ^{19}F nmr, infrared and Raman spectra. Vapor density; Found 334, calc. 339 g/mol. Vapor pressure-temperature data for this mixture were recorded (T°C, P_{mm}): -31.9, 3.5; -26.1, 5; 0.0, 21; 10.4, 34; 17.6, 46; 20.7, 54. For the range -32 to 20°C log P_{mm} = 7.1578-1595.4/T°K with a calc. b.p. = 100°C and ΔH_v = 7.30 kcal/mol.

Reaction of SF_5OF with $ClCF{=}CFCl$.

A prepassivated, evacuated, 30 ml cylinder was cooled to -196°C and loaded successively with $ClCF{=}CFCl$ (3.01 mmol) and SF_5OF (2.14 mmol) from the vacuum line. The cylinder was allowed to warm slowly to -78°C using a liq. N_2-CO_2 slush and then to ambient temperature. After 2d the products were separated by fractional condensation in U-traps cooled to -45, -78, and -196°C. The adduct obtained, $SF_5OCFClCF_2Cl$, (1.65 mmol, 77% yield) was identical to that prepared using SF_5OCl and $CF_2{=}CFCl$.

RESULTS AND DISCUSSION

SF_5OHal was successfully added to highly fluorinated olefins according to:

$$SF_5OCl + CF_2{=}CFH \longrightarrow SF_5OCF_2CFHCl \qquad 44\% \text{ yield}$$

$$\begin{tikzcd} SF_5OCl + CF_2{=}CFCl \arrow[dr] & & 50\% \\ & SF_5OCFClCF_2Cl & \\ SF_5OF + ClCF{=}CFCl \arrow[ur] & & 77\% \end{tikzcd}$$

$$SF_5OCl + CF_2{=}CFBr \longrightarrow SF_5OCFBrCF_2Cl + SF_5OCF_2CFBrCl \qquad 59\%$$

77% + 23% isomer mixture

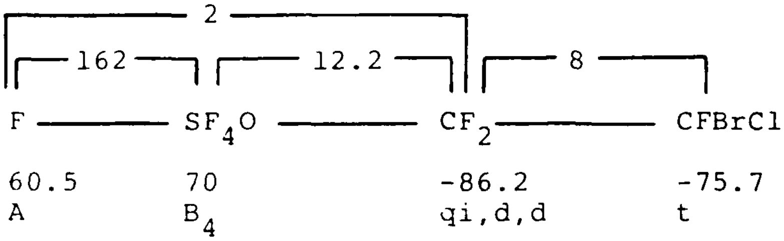
These reactions required careful control. For example when $CF_2{=}CFBr$ was added fairly rapidly to SF_5OCl at -78°C, the yield of SF_5OR_f fell significantly. The principal by-products were SF_4O and chloro-fluorinated adducts. All of the SF_5O- substituted fluorocarbons are thermally stable, storable, clear, colorless liquids of moderate volatility.

The observed modes of addition for SF_5OCl are in general agreement with an electrophilic chlorine attacking the olefins as described for the analogous reactions of CF_3OCl [7]. However the finding of one isomeric adduct only in the case of $CF_2{=}CFCl$ was surprising since both the above mentioned CF_3OCl gave both isomers [3,4] as did FO_2SOCl [8]. No simple explanation is apparent for this difference.

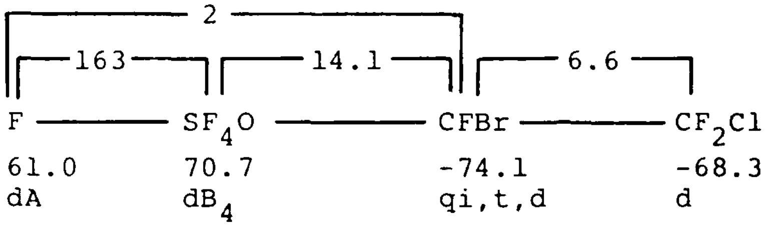
Table 1 lists the ^{19}F and ^{1}H nmr data for the new compounds. The magnetic inequivalence of the axial fluorine compared to the four basal fluorines in the SF_5O group gives rise to AB_4 type spectra. Chemical shifts and coupling constants are typical of those for similar SF_5O- carbon compounds [2,9]. In highly halogenated derivatives the chemical shift of the apical F on sulfur is upfield from that of the basal SF_4 group whereas in the hydrogen containing compound it appears downfield. This is also observed for the chemical shifts of related AB_4 patterns from SeF_5O- [10] and TeF_5O- [11] substituted fluorocarbons. The first order CF and CH parts of the spectra allowed unambiguous determination of the isomer or isomers present and the measurement of the isomer ratio in the latter case.

Vibrational spectral data are given in Table 2. The strong infrared bands in the region 1300-950 cm^{-1} are characteristic for C-F and C-O stretching motions. For all the SF_5O- compounds intense infrared bands were found at about 930, 880, and 600 cm^{-1} which are attributable to $\nu_{as}SF_4$, $\nu SF'$ and $\delta_s SF_4$, respectively, of the SF_5O- group. These assignments correspond closely to those given for other SF_5- containing molecules [12,13]. Raman counterparts exist for many of these infrared bands, although they are, as expected, of relatively low intensity, especially for the C-F and C-O vibrations. The Raman spectra are generally dominated by a polarized band near 730 cm^{-1} which is assigned to the symmetric SF_4 stretching mode, and which has no infrared counterpart. Other tentative assignments appear in Table 2. All of the spectral data agree with the formulation of these compounds shown earlier.

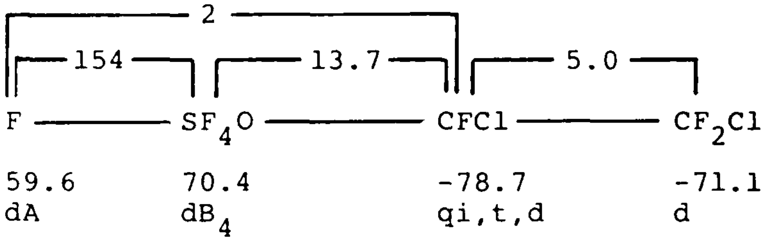
TABLE 1. ^{19}F NMR DATA FOR R_fOSF_5 COMPOUNDS[a]



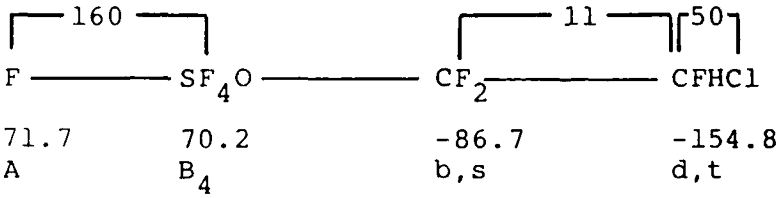
F	SF_4O	CF_2	CFBrCl
60.5	70	-86.2	-75.7
A	B_4	qi,d,d	t



F	SF_4O	CFBr	CF_2Cl
61.0	70.7	-74.1	-68.3
dA	dB_4	qi,t,d	d



F	SF_4O	CFCl	CF_2Cl
59.6	70.4	-78.7	-71.1
dA	dB_4	qi,t,d	d



F	SF_4O	CF_2	CFHCl
71.7	70.2	-86.7	-154.8
A	B_4	b,s	d,t

$\delta = 5.9d(J_{HF}-49)$

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[a] $CFCl_3$ reference, negative shift being upfield from the reference, ϕ = chemical shift, ppm. J=Hz, where b=broad, s=singlet, d=doublet, t=triplet, qi=quintet. The area ratios measured for these resonances agreed with the given assignments.

TABLE 2. VIBRATIONAL SPECTRA OF R_fOSF_5 COMPOUNDS

Obsd. Freq., cm^{-1} (rel. intens.)[a]

	SF_5OCF_2CFHCl		$SF_5OCFClCF_2Cl$		$SF_5OCFBrCF_2Cl/SF_5OCF_2CFBrCl$	
Assign.[b]	IR(gas)	Raman(liq.)	IR(gas)	Raman(liq.)	IR(gas)	Raman(liq.)
νCH	2995 vw	3005(0.5)dp				
δCH	1360 m	1365(0.3)				
		1290(0.3)				
	1270 m	1275(0.3)			1255 vw	
	1252 m	1255(0.4)dp	1245 m	1248(0.5)dp	1235 w	1240(0.3)dp
νCF	1175 vs	1175(0.2)	1190 s	1185(0.2)	1185 s	1180(0.1)
		1145(0.4)	1145 sh	1140(0.2)	1150 sh	
	1140 vs		1130 s		1130 s	1135(0.1)
	1105 s	1105(0.4)	1115 sh	1110(0.2)	1110 sh	1105(0.3)p
νCO	1035 w			1045(0.9)p	1030 ms	1028(2.7)p
νCC	945 vs	930(0.4)	950 vs	955(0.2)	948 vs	950(0.2)
$\nu_{as}SF_4$	930 vs	915(0.3)	930 vs	915(0.2)	930 vs	925(0.1)
νSF'	863 s	865(0.7)p	885 s		890 vs	890(0.3)
δCF_2	825 s	825(3.2)p	845 m		813 m	870(0.3)
νCCl		775(3.3)p	785 m	782(0.7)p		775(1.3)p
νSO	755 m	760(4.2)p	758 w	745(1.8)p	735 w	745(4.2)p
ν_sSF_4 ip		745(10)p		730(10)p		725(10)p
	732 w	730(6.6)	722 m		718 w	
				685(0.4)p		690(0.4)p
				660(0.9)p		655(1.0)
$\nu_sSF_4$op		640(1.2)p	630 vw	640(1.6)		635(2.2)p
		615(0.8)p		615(1.1)p		605(1.1)p
$\delta_sSF_4$opl	600 ms	605(0.7)dp	600 s	605(0.4)dp	605 s	590(0.5)
	575 w	575(0.9)p				
	555 vw	555(0.9)p		547(0.6)p	535 vw	535(0.5)p
		520(0.6)p		525(0.8)dp	500 vw	515(0.8)p
		485(1.3)p		490(1.2)p		
		468(1.2)		470(0.8)p		475(1.5)p
		445(2.2)p		448(4.3)p		448(4.7)p
		430(2.8)p		420(1.5)p		
		380(1.0)				372(2.3)p
		355(0.7)p		350(0.8)		350(1.0)
		315(0.7)		310(1.1)		318(3.7)p
				290(0.9)		295(2.9)p
		278(1.4)p		275(2.0)p		275(1.7)p
		235(1.9)p		230(1.0)		238(5.0)p
		210(1.7)p		215(1.5)p		215(5.4)p
		185(2.0)p		185(1.5)p		180(1.4)p
						165(0.8)p
						145(1.1)dp

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[a] Uncorrected Raman intensities (peak heights)

[b] *ip* = *in phase; op* = *out of phase; opl* = *out of plane*

Numerous attempts were made to dehalogenate $SF_5OCFClCF_2Cl$, and also $SF_5OCFBrCF_2Cl$ in its isomer mixture, in order to obtain the unknown $SF_5OCF=CF_2$. Conditions similar to those employed for the analogous reaction of $CF_3OCFClCF_2Cl$ to give $CF_3OCF=CF_2$ [14] were used. Those authors noted that dimethyl sulfoxide was the only successful solvent for the dehalogenation. We were unsuccessful in our efforts using DMSO, diglyme, dioxane, or DMF solvents with Zn powder (activated) or Zn-Cu couple at temperatures up to 140°C. No olefinic material was obtained and increasing degradation of the starting material was noted at higher temperatures and longer reaction times. Ultrasound activation with DMSO/Zn at 45°C gave similar results. In the absence of a solvent these two SF_5OR_f compounds could be heated with Zn to 195°C for 4 days and not be affected.

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